

## CHEMISORPTION OF NITRIC OXIDE ON CHAR: KINETICS AND MECHANISM

Hsisheng Teng and Eric M. Suuberg

Division of Engineering  
Brown University  
Providence, Rhode Island 02912

**Keywords :** Nitric Oxide, Carbon, Chemisorption, Active Sites

### INTRODUCTION

The reactions of nitric oxide with carbons have been considered as offering interesting possibilities for reduction of NO emissions from combustion systems. Some of the relevant literature on these reactions has been reviewed in a paper on the global kinetics of the gasification reaction<sup>1</sup>. The first step of the process, involving the chemisorption of NO on the carbon surface, has been separately considered<sup>2</sup>. The literature on chemisorption and/or physisorption of NO on carbons is limited<sup>3-15</sup>. Most of these studies acknowledge that if temperatures are kept low (i.e. well below ambient) mainly physisorption occurs<sup>5,8,10</sup>. It is generally agreed that chemisorption occurs to a significant extent at temperatures above ambient. The chemisorption is generally accompanied by formation of surface oxides and release of N<sub>2</sub>. Beyond this, the nature of the chemisorption process remains somewhat of a mystery.

One study has reported that the chemisorption of nitric oxide affects the spin-resonance absorption of charcoal in a manner similar to oxygen; there is an increase of ESR absorption linewidth with increasing extent of absorption on a cleaned carbon surface<sup>12</sup>. The difference is that oxygen adsorbed at room temperature can be desorbed by evacuation, whereas nitric oxide cannot. The initial absorption appears, on the basis of magnetic susceptibility, infrared, and thermal studies, to involve the addition of nitric oxide in an "N-down" configuration<sup>5,6</sup>. Another study cast doubt on the notion that the sites reactive towards nitric oxide addition could be spin centers<sup>4</sup>. It also appeared that more highly heat-treated carbons gave nitric oxide surface complexes of lower thermal stability<sup>4</sup>. This suggests that addition to aromatic ring structures is involved, and that the number of resonance structures affects the stability of the NO adduct. In short, it appears that the literature implies that radical addition processes occur on the surface of carbons, involving the paramagnetic nitric oxide (which is essentially free radical in nature). These addition processes appear to affect the ESR spectra, but do not destroy the measurable free radicals in carbons (which are probably of the  $\pi$  type). Thus the addition process does not appear to involve the "titration" of the measurable radicals in carbon by the nitric oxide. Hence the identity of the "active sites" in carbon remains unclear. The present measurements shed some new light on these issues.

### EXPERIMENTAL

A standard thermogravimetric analyzer (TGA) was used for studying the kinetics of NO chemisorption on chars. Experiments were performed in a static gas environment, in He/NO mixtures at 101 kPa total pressure. The volume of the vessel was large enough to ensure that under any reaction conditions, the consumption of NO was not significant. Pulverized char samples

(50–100 mg) were held in a quartz bucket suspended in the heated zone of a quartz tube. A thermocouple placed within a few millimeters of the bucket served to indicate its temperature. The vessel could be purged following experiments, and the contents analyzed by gas chromatography.

The chars used in present study were derived from phenol-formaldehyde resins. These resins were synthesized in house in order that they contain few catalytic impurities (< 200 ppm)<sup>16</sup>. The resin char was prepared by pyrolysis of the phenol-formaldehyde resin in a helium environment at 1323 K for 2 hours, then ground and sieved to give the desired particle size. The surface of the char was cleaned of oxides prior to NO sorption experiments by heating the sample to 1223 K in extra high purity helium for at least 2 hours. NO sorption experiments were performed after surface cleaning by lowering the temperature of the sample from 1223 K to the desired sorption temperature, and then quickly introducing the desired NO/He mixture.

In order to clarify the mechanism of NO sorption on char, information on surface species formation during the course of sorption is required. Since N<sub>2</sub> and CO, both with a molecular weight of 28, are released during the thermal desorption of products from NO oxidized carbon, mass spectrometry could not be used for gas analysis. This required the use of gas chromatography (GC) as the main analytical technique. Thus temperature programmed desorption (TPD) experiments, with a linear heating rate of 22.5 K/min, were carried out in a TGA/GC system. TPD of NO treated chars were performed from 473 to 1223K. The desorbed gas products, purged from the TGA by helium, were collected in a cryogenic trap of Porapak-QS polymer kept at liquid-nitrogen temperature (77 K). This was necessary to boost product concentrations to conveniently measurable levels, as the concentrations within the TGA ambient gas were very low. The products could be desorbed from the trap by raising its temperature to ambient. Quantitative measurements of the products were performed on a Hewlett Packard GC equipped with a 2.1-m column of molecular sieve 5A. Significant amounts of NO were found to non-dissociatively adsorb on carbon surface at temperatures lower than 473K. The analysis of NO by this technique is not quantitatively reliable, but from the data on sample mass and GC analysis of other products, the quantity of NO desorbed during TPD could be evaluated from a mass balance. The surface species formed on chars were studied as a function of NO pressure, time, and temperature.

Specific surface areas of the samples were determined by the N<sub>2</sub> BET method at 77 K. A standard flow-type adsorption device (Quantasorb) was employed for the measurements. Prior to any such analysis, samples were outgassed in flowing N<sub>2</sub> at 573 K for 3 hours.

## RESULTS AND DISCUSSION

The mass uptake curves obtained during chemisorption of NO on a cleaned char surface are shown in Figure 1, and as we have reported earlier, follow so-called Elovich sorption kinetics<sup>2</sup>:

$$r_{ad} = dq/dt = b \cdot \exp[-a \cdot q] \quad (1)$$

where  $r_{ad}$  is the rate of sorption,  $a$  and  $b$  are fitting parameters, and  $q$  is the amount of mass uptake per unit of BET surface area. The values of  $a$  and  $b$  under different chemisorption conditions are given in Table 1. The value of  $a$  is a function of chemisorption temperature in NO sorption on char (as it is in O<sub>2</sub>, e.g. ref 17,18). The value of  $a$  is generally a decreasing function of chemisorption temperature in the case of O<sub>2</sub> chemisorption. It is an increasing function of temperature in NO chemisorption. An increasing value of  $a$  with increasing chemisorption temperature can lead to a negative apparent activation energy for chemisorption, based on the following equation:

$$d\ln(r_{ad})/d(1/T) = -E_{ad}/R = d(\ln b)/d(1/T) - [da/d(1/T)] \cdot q \quad (2)$$

where  $E_{ad}$  is the apparent activation energy for chemisorption. The first term is positive (see below) and the second term is negative, implying that  $E_{ad}$  must be negative. The increase of the value of  $a$  with increasing chemisorption temperature in the case of NO chemisorption has been attributed to the occurrence of exothermic reversible NO sorption which would result in less mass uptake at higher temperature<sup>2</sup>. The overall NO sorption reaction is actually a combination of reversible and irreversible process, *vide infra*, and cannot be simply represented by (1) or (2).

The physical significance of the parameter  $b$  is that it represents the initial rate of mass uptake on the clean char surface. At constant temperature, it is seen from Table 1 that the value of the parameter  $b$  increases with increasing NO pressure, as might be expected from a surface collision controlled process. This result is similar to that of O<sub>2</sub> chemisorption reported by other workers<sup>18</sup>. In the case of NO chemisorption, however, the  $b$  value decreases with increasing chemisorption temperature. This would also imply a negative activation energy for the initial chemisorption, again because of the reversible nature of NO uptake<sup>2</sup>. In short, Elovich-type analyses may provide satisfactory curve fitting for the NO-carbon system, but they are of no physical significance.

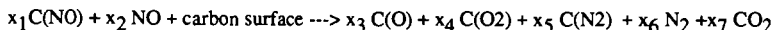
The existence of a certain amount of reversible sorption of NO has been earlier established<sup>2,3</sup>. We showed that such chemisorption data imply a heat of reversible chemisorption of -42 kJ/mol (i.e. exothermic)<sup>2</sup>. A heat of reversible NO adsorption on graphite of around -70 kJ/mole has been reported by others<sup>6</sup>. These values indicate chemisorption, since they are much higher than those for ordinary physisorption, which are usually less than 20 kJ/mol exothermic. The process can be represented in thermodynamic terms by<sup>2</sup>:



This process of reversible sorption of NO is however accompanied by irreversible surface reactions involving NO. Moreover the thermodynamic representation of the reaction (R1) does not correctly portray the kinetics of this process, as discussed below.

#### Surface Complexes Involved in NO Chemisorption on Char

Once C(NO) is formed, it can react via thus far unestablished mechanisms to give other irreversibly bound surface species. This process can be generally represented by:



The choice of the symbols on the right hand side is based on the experiments used to identify surface products. The symbol C(N<sub>2</sub>) represents the surface species that result in release of N<sub>2</sub> during post-chemisorption TPD. Likewise, CO is said to come from C(O), CO<sub>2</sub> from C(O<sub>2</sub>), and NO from C(NO). No particular structures or desorption mechanisms are implied by this nomenclature; it is selected for convenience alone. Both N<sub>2</sub> and CO<sub>2</sub> can evolve during chemisorption. The CO<sub>2</sub> is measured by GC, at the end of chemisorption. The N<sub>2</sub> is determined by mass and element balance, based upon the results of the post-chemisorption TPD analysis. The results of these analyses, following different times of sorption under 10.1 kPa of NO at 323 and 373 K, are shown in Figs. 2 and 3, in units of g/m<sup>2</sup>. No other products are seen.

The amount of N<sub>2</sub> forming complexes, C(N<sub>2</sub>), remained roughly constant on the char surface

throughout chemisorption at  $0.98 \cdot 10^{-4} (\pm 0.12 \cdot 10^{-4})$  and  $0.76 \cdot 10^{-4} (\pm 0.10 \cdot 10^{-4})$  mmole/m<sup>2</sup> for 323 and 373 K, respectively. Although the sites for C(N<sub>2</sub>) have been saturated at these chemisorption conditions, the number of C(N<sub>2</sub>) complexes on the char surface under these conditions is still less than that during steady state gasification ( $\sim 3.6 \cdot 10^{-4}$  mmole/m<sup>2</sup>)<sup>1</sup>. Since in the low temperature chemisorption regime, C(N<sub>2</sub>) decreases with increasing temperature, the higher value at the higher gasification temperatures cannot be predicted by simple extrapolation of the low temperature chemisorption results. It is likely that C(N<sub>2</sub>) complexes are created by different mechanisms during gasification at higher temperatures.

We believe that C(N<sub>2</sub>) actually involves dissociated N atoms on the surface, because of the high desorption temperatures needed to release most of this product (>900K). These are relatively minor surface species, and because we observe them to form very quickly (virtually all before the first surface species measurements), they may be formed at exceptionally active surface sites on the freshly cleaned char surface. We cannot necessarily rule out the possibility that this surface species quickly builds up to a static concentration as a result of a fast dynamic equilibrium involving its formation and destruction, but this seems unlikely since the kinetics of release of N<sub>2</sub> during chemisorption (see Figs. 2 and 3) appear to be too slow to support such a dynamic equilibrium.

In contrast to C(N<sub>2</sub>), both C(O) and C(O<sub>2</sub>) both increase in concentration throughout chemisorption (see Figs. 2 and 3). The C(O<sub>2</sub>)/C(O) ratio on char surface is not constant during chemisorption and at 323K increases from 0.27 (molar basis) after 0.2 hour of chemisorption to 0.52 after 24 hours. For 373 K chemisorption in 10.1 kPa NO, the C(O<sub>2</sub>)/C(O) ratio increases slightly with reaction time from 0.22 after 0.2 hour to about 0.27 after 1.6 hours and remains constant afterwards. The C(O<sub>2</sub>)/C(O) ratio of 373 K sorption is less than that of 323 K sorption. The increasing C(O<sub>2</sub>)/C(O) ratio of surface species with decreasing reaction temperature is in agreement with the fact that the CO<sub>2</sub>/CO ratio decreases with increasing steady state gasification temperatures<sup>1</sup>. The TPD results have revealed that the CO<sub>2</sub> desorption product evolves at lower temperatures than the CO desorption product. In fact, the formation of gaseous CO<sub>2</sub> product is significant during chemisorption at 373 K, but was too low to be accurately measured at 323 K (see Figs. 2 and 3). Considering the sum of C(O<sub>2</sub>) plus desorbed CO<sub>2</sub> in the case of the 373 K sorption, this value is actually seen to be quite similar to the value for C(O<sub>2</sub>) alone at 323 K, at all times. The weak temperature dependence in the kinetics of formation of the total C(O<sub>2</sub>) complexes implies that there is a process of moderately low activation energy responsible for the conversion of other surface intermediates to C(O<sub>2</sub>). The apparently strong temperature dependence of the actual C(O<sub>2</sub>) population actually reflects the temperature dependence of desorption of CO<sub>2</sub>.

The population of C(O) on char is a weak function of sorption temperature, and is seen to slightly decrease with increase in temperature, for any time of measurement. The total yield of all irreversible C(NO) decomposition products, i.e. C(N<sub>2</sub>), C(O) and C(O<sub>2</sub>) surface complexes plus released gaseous CO<sub>2</sub>, is relatively constant after 24 hours, for any given temperature within this range (15.4 and 14.4 mmol/m<sup>2</sup> for 323 and 373 K, respectively). One might expect that when CO<sub>2</sub> is desorbed in the 373 K case it would leave an "active site" behind that could gain further oxygen by the same mechanism as before, but this does not appear to happen. This implies that the surface appears to "heal" itself upon CO<sub>2</sub> desorption, and that active sites are not regenerated by desorption at these temperatures (This conclusion does not hold when higher temperatures are involved; TPD of this char following NO exposures up to gasification conditions shows the oxide population to be an increasing function of temperature<sup>19</sup>).

Since the total population of surface species changes little with time beyond about 24 hours, the behavior in NO chemisorption is quite different from that in O<sub>2</sub> chemisorption. In O<sub>2</sub>, the total number of complexes quite commonly continues to increase indefinitely, until the rate of desorption begins to overtake the rate of chemisorption. In NO, it appears that there is only a particular inventory of sites that can be filled, at any temperature. What limits the inventory is unclear. The fact that the total uptake of irreversibly held species is only a weak function of temperature suggests that certain types of structures initially exist within the carbon, and that they alone are capable of participating in the formation of dissociation products.

The mass of chemisorbed oxygen atoms on the char surface can be converted to a surface area occupied by these oxygen atoms, by applying the assumption<sup>20</sup> that each oxygen atom occupies an area of  $8.3 \cdot 10^{-20}$  m<sup>2</sup>. The surface area occupied by oxygen atoms of any released CO<sub>2</sub> before its desorption from the char surface is taken into account. This surface area is obviously a weak function of chemisorption temperature and constitutes  $0.094 \pm 0.003$  of the total surface area (TSA = 320 m<sup>2</sup>/g) of the sample, under the conditions at which the surface oxide inventory was measured (18% burnoff char). In the case of oxygen chemisorption on this same char, the surface area occupied by oxygen atoms is an increasing function of chemisorption temperature, accounting for 0.032 of TSA at 373 K and 0.046 at 473 K. Different numbers of "active sites" are thus apparently involved in NO and O<sub>2</sub> chemisorption, although this comparison is perhaps unfair in that the carbons on which oxygen ultimately resides may not be the same as the carbons involved in the initial chemisorption. It should also be mentioned that in the case of NO, there is a strong suggestion that the micropore surface area is not fully accessible<sup>19</sup>, so the value of 0.094 may actually underestimate the fraction of accessible surface that is covered. A similar accessibility problem was not observed with O<sub>2</sub>.

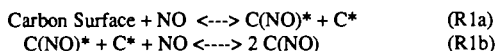
#### The Kinetics of Surface Complex Formation

The formation during chemisorption of each of the different types of surface complexes can be described by the Elovich equation (1) and the fitting parameters *a* and *b* for the different complexes are shown in Table 2. Again, comments similar to those related to those for total mass uptake may be made with respect to these (note trends with temperature). In this case, however, the *b* parameter provides some useful insights into the process. The *b* value is about an order of magnitude higher for the formation of C(O) than that for C(O<sub>2</sub>) at 323 K. Since *b* is the initial rate of complex formation, the relative magnitudes of these values apparently imply that the C(O) complexes are created earlier. This in turn suggests that some of them could serve as reactive intermediates on the char surface, and can react with NO from the gas phase or C(NO) on carbon surface, to generate the C(O<sub>2</sub>) complexes. The hypothesis that C(O<sub>2</sub>) is derived from C(O) has been advanced earlier<sup>11</sup>.

At 323 K, the formation of reversibly adsorbed NO (i.e. C(NO)) is slightly more rapid than other surface species (see Table 2). Thus it seems to support the very plausible notion that the C(NO) surface complex may serve as an initial intermediate. Such an initial step for NO-carbon chemisorption was also proposed by previous workers<sup>4,10</sup>. It is unclear how the kinetics of formation of other surface species should depend on C(NO) concentration ([C(NO)]), or on the partial pressure of NO in gas phase (one or the other must be involved, based upon stoichiometric considerations). Reactions were performed at 323 K under different NO pressures to explore this

dependence. By back extrapolation of these data to zero time, the rates of complex formation on clean char surface under different NO pressures were determined.

The initial rates of C(NO) formation ( $r_0$ ) on clean char surface under different NO pressures are shown in Fig. 4. It was found that the reaction of C(NO) formation on clean surface is close to second order with respect to NO pressure. Thus the reaction (R1) does not accurately portray the kinetics of this step. We hypothesize that the addition of NO occurs in a process that can be represented in two steps:



where C(NO)\* is an unstable NO addition product, C(NO) is the stable product, and C\* represents the odd electron contributed to the carbon structure by the first NO addition step. It is hypothesized that the odd electron must be paired with a second electron, in order to make two surface complexes stable. This is the origin of the second order. Note that overall, the concentration of C(NO) would still be proportional to NO partial pressure, as in (R1).

There was little C(NO) on the clean char surface initially, and it was impossible to establish the role of C(NO) in the reactions for C(O) and C(O<sub>2</sub>) formation on the clean surface by the same kind of back extrapolation to zero time. Thus the rates of C(O) and C(O<sub>2</sub>) formation were evaluated, at particular extents of total oxide surface coverage to clarify the role of C(NO) in the reaction. It was found that the rate of C(O) formation was approximately first order with respect to C(NO) and simultaneously second order with respect to gas phase NO. Thus, the process appears to be limited by the ability to form a second stable complex in the vicinity of a first stable C(NO) complex.

As for the formation of C(O<sub>2</sub>), the rate might be expected to be related to the population of C(O) on the char surface. Therefore rates of C(O<sub>2</sub>) formation were examined at constant [C(O)]. It was found that the rate was first order with respect to both C(NO) and C(O), and second order with respect to NO in the gas phase. Again, the suggestion is that the placing of a stable C(NO) complex near to existing surface complexes is a key limiting step.

## CONCLUSIONS

The chemisorption of NO on char surface is not always immediately followed by the release of N<sub>2</sub> from the dissociation of the NO molecule. Reversibly (i.e. C(NO)) as well as irreversibly bound complexes (i.e. C(O), C(O) and C(N<sub>2</sub>)), can all exist on the char surface. The reversible sorption of C(NO) on a resin char surface is an exothermic reaction having an enthalpy of -42 kJ/mole. The rate of C(NO) formation on clean char surface is roughly second order with respect to NO pressure, but [C(NO)] is proportional to NO pressure at equilibrium. The mechanism for C(O) and C(O<sub>2</sub>) formation appears to involve both gaseous NO and C(NO) complexes. The formation of stable C(NO) surface complexes is hypothesized to involve an electron-pairing mechanism, and is important in the formation of irreversibly bound surface complexes as well.

## ACKNOWLEDGEMENT

The financial support of the U. S. D.O.E. (grant DE-FG22-87PC79929) and the Exxon Education Foundation are gratefully acknowledged.

# REFERENCES

1. Suuberg, E.M., Teng, H. and Calo, J.M., 23rd Symposium (Int.) on Combustion, The Combustion Institute, in press (1990-91).
2. Teng, H., Suuberg, E.M., and Calo, J.M., ACS Div. Fuel Chem Prepr., **35**(3), 592 (1990).
3. DeGroot, W.F., Osterheld, T.H., and Richards, G.N., Carbon, **29**, 185 (1991).
4. Harker, H., Gallagher, J.T., and Parkin, A., Carbon, **4**, 401 (1966).
5. Zarifyanz, Y.A., Kiselev, V.F., Lezhnev, N., and Nikitina, O., Carbon, **5**, 127 (1967).
6. Zarifyanz, Y.A., Russian J. of Physical Chemistry, **38**, 1439 (1964).
7. Smith, R.N., Swinehart, J., and Lesnini, D., J. Phys. Chem., **63**, 544 (1959).
8. Smith, R.N., Lesnini, D., and Mooi, J., J. Phys. Chem., **60**, 1063 (1956).
9. Shah, M.S., J. Chem. Soc., 2661 (1929).
10. Brown, C.E. and Hall, P.G., Trans. Faraday Soc. **67**, 3558 (1971).
11. Brown, C.E. and Hall, P.G., Surface Science, **30**, 379 (1972).
12. Pastor, R., Weil, J., Brown, T., Turkevich, J., Adv. in Catalysis, **9**, 107 (1957).
13. Richter, E., Kleinschmidt, R., Pilarczyk, E., Knoblauch, K., Jüntgen, H., Thermochemica Acta, **85**, 311 (1985).
14. Richter, E., Chem.-Ing.-Tech., **55**, 986 (1983).
15. Cascarin de Torre, L.E. and Arvia, A.J., An. Quim. **64**, 349 (1968).
16. Suuberg, E.M., Wójtowicz, M., and Calo, J.M., 22nd Symposium (Int.) on Combustion, The Combustion Institute, 79 (1988).
17. Khan, M.R., Everitt, C.E., and Lui, A.P., Comb. and Flame, **80**, 83 (1990).
18. Bradbury, A.G.W. and Shafizadeh, F., Carbon, **18**, 109 (1980).
19. Manuscript in preparation.
20. Laine, N.R., Vastola, F.J. and Walker, P.L., Jr., J. Phys. Chem., **67**, 2030 (1963).

Table 1. The Elovich parameters for NO chemisorption on char- total mass uptake

Pressure (kPa)	10.1				4.04	2.02
Temperature (K)	473	423	373	323	323	323
a [ $\text{m}^2/\text{g}$ ] $\cdot 10^{-6}$	0.265	0.249	0.225	0.0811	0.117	0.149
b [ $\text{g}/\text{m}^2\text{hr}$ ] $\cdot 10^6$	53.5	86.1	221	337	69.8	16.0

Table 2. The Elovich parameters for formation of surface complexes.

	C(O <sub>2</sub> )	C(O)	C(NO)
<u>T = 323 K</u>			
a $\cdot 10^{-6}$	0.213	0.248	0.147
b $\cdot 10^6$	19.4	155	211
<u>T = 373 K</u>			
a $\cdot 10^{-6}$	0.474	0.240	0.658 <sup>†</sup>
b $\cdot 10^6$	16.8	71.5	96.8

a is in  $\text{m}^2/\text{g}$ , and b is in  $\text{g}/(\text{hr}\cdot\text{m}^2)$       † 1.6 hours of chemisorption

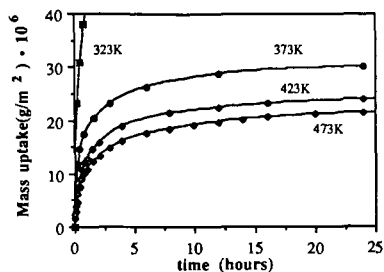


Fig. 1 Total mass uptake as a function of time in chemisorption under 10.1 kPa NO pressure.

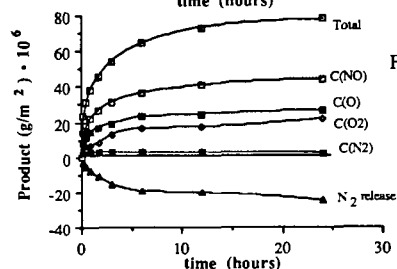


Fig. 2 Product formation during 323K chemisorption under 10.1 kPa of NO (mass of carbon not included in C(NO) and C(N₂) values).

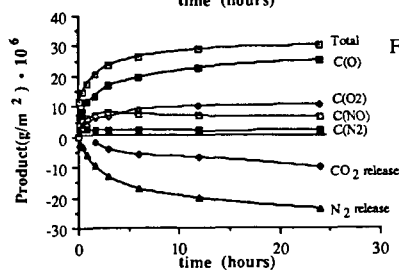


Fig. 3 Product formation during 373K chemisorption under 10.1 kPa of NO (mass of carbon not included in C(NO) and C(N₂) values).

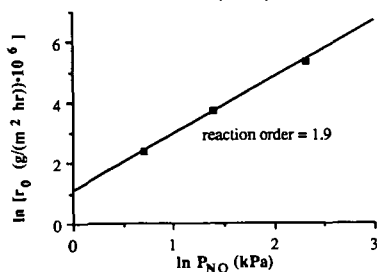


Fig. 4 Initial rate of C(NO) formation on clean char surface under different NO pressures.